KINETICS OF LIGNITE CHAR GASIFICATION
- ITS RELATION TO THE CO_2 ACCEPTOR PROCESS

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INTRODUCTION

The basic features of the CO_2 acceptor gasification process have been described in a series of recent publications. The general nature of the process was described, heat and material balances presented,[1,2,3] and the operating limitations of the process as determined by the thermodynamic properties of individual reactions of importance were discussed.[1] A more detailed discussion of the properties of dolomite and limestone based acceptors as dictated by the needs of the process was presented in a more recent publication.[4]

Due to thermodynamic limitations of the acceptor reactions, the maximum permissible temperatures and pressures for operation of the gasifier are approximately 1670°F and 380 psia, respectively. In general, it is desirable to operate the process below these extreme limits.

The kinetics of the gasification of chars from Pittsburgh Seam bituminous coals had been studied in some detail previously.[5] The gasification rates obtained are likely adequate for operation of the CO_2 acceptor process with bituminous coal chars provided partial gasification is practiced with low sulfur boiler fuel[6] as a byproduct. The gasification rates are, however, inadequate for total gasification of bituminous coal chars.

The emphasis on the development of the CO_2 acceptor process has, therefore, been on the use of lower rank Western coals, and in particular lignite chars, because their known higher reactivity makes them more suitable for the process.

The experimental techniques and methods of processing the data will be only briefly described here. Full details will be available in a report to be submitted to the Office of Coal Research in the near future.

Experimental and Calculational Procedures

Integral Batch Kinetics

The data were obtained in a fluidized bed unit which was operated batchwise with respect to solids and continuously with respect to the gas feed. The unit is illustrated schematically in Figure 1.

Char feedstocks were prepared by carbonizing the raw, dried lignites in N_2 at 1050°F at atmospheric pressure. The chars were devolatilized further by heating in a fluidized bed in H_2 at 1400°F for one hour at atmospheric pressure. The latter treatment also calcined the $CaCO_3$ and reduced the iron compounds which were present in the ash. The 35 x 65 mesh size fraction was used. Analyses of the prepared lignite chars are given in Table Ia.

Most of the runs were made with one of two initial char bed weights of either 5 or 10 grams. The char was mixed with 200 x 325 mesh fused periclase in order to hold a nearly constant fluidized bed height of 2-1/2 inches, regardless of the initial char weight or burnoff level.

The reactor consisted of a 7" x 1" I.D. Type 310 stainless steel thin-walled tube having a conical sealed end. The reactor with its heating elements and insulation was contained within a pressurized one-liter autoclave. Nitrogen was used as pressure balancing gas.

The temperature control point was a calibrated thermocouple contained in a well immersed in the fluidized bed. Axial traverses showed that the temperature throughout the bed was $1500° \pm 2°F$.

The inlet dry gases were preblended mixtures of H_2, CO, CO_2 and CH_4 in the desired proportions. The metered dry gas was passed through a steam generator in which the water temperature was controlled ($\pm$ 0.2°F) to give the desired steam partial pressure. CO_2 was added to the dry gas mixtures in order to bring the composition of the total inlet gas to water-gas shift equilibrium. Otherwise, the partial pressures of the inlet H_2O, H_2 and CO would have been altered appreciably by shifting, catalyzed by the reactor surfaces and the char bed.

The total inlet gas entered the reactor through an axial diptube which extended to the bottom of the cone. The gas passed downward, reversed direction, and fluidized the bed. The superficial fluidizing velocity was held in the range, 0.14-0.18 ft/sec depending on the pressure level and gas composition in order to give a bed expansion of about 30% over the incipient fluidized bed height.

The exit gas was cooled to condense the unreacted steam, which was then throttled to atmospheric pressure and collected in the condensate receiver. The dry exit gas, after being throttled to atmospheric pressure, passed through the condensate receiver to pick up the dissolved gases which had flashed from the condensate. Most of the H_2S was removed by an acidified $Cd(NO_3)_2$ solution which had been charged initially to the condensate receiver. One side stream of the dried gas was diverted through a sample loop where, typically, a sample was taken every 12 minutes for analysis by gas chromatography. Another was diverted through a thermal conductivity cell which continuously monitored the exit gas composition in reference to the inlet dry gas. The diverted streams were recombined, saturated with water, and passed through a calibrated wet test meter.

In the runs where the inlet dry gas contained carbon oxides and/or CH_4, the dual-column gas chromatograph was operated differentially. Samples of the inlet dry gas and exit gas were simultaneously injected into their respective columns and the outputs of the thermal conductivity detector cells were arranged to give signals which were proportional to the differences in concentrations of CO, CO_2, and CH_4 in the two gas streams.

In all the runs the char was pretreated by fluidizing in pure H_2 for one hour at 1400°F and at 6 atm system pressure. During this period, 8.0% of the carbon in the feed char was reproducibly gasified.

The kinetics portion of the run was then started by raising the system pressure to the desired level, increasing the bed temperature to 1500°F, and replacing the hydrogen flow with the desired flows of steam and inlet dry gas. These operations, performed in the order given, were completed in about one minute.

At the end of a run the bed was rapidly cooled and removed from the reactor. The entire bed, i.e., char plus diluent was assayed for its carbon content.

It was found necessary to presulfide the reactor and char bed to eliminate spurious effects due to catalytic formation of methane or its hydrolysis, depending upon which side of equilibrium the gas composition in the reactor corresponded to in the reaction

$$CO + 3 H_2 = CH_4 + H_2O \tag{1}$$
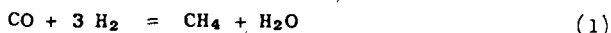
With a presulfided system, all methane produced was derived from gasification of the char. Presulfiding was accomplished by passing a 1% H_2S-99% H_2 mixture through the system for one hour at 1200°F and at atmospheric pressure before the pretreatment period was started.

The integral gasification rates at time Θ reported here are defined below:

$$R_T = \frac{\text{total mols of carbon gasified/min x } 10^4}{\text{atom of carbon in bed}} = \frac{N \text{ x } 10^4}{w_o - \int_o^\Theta Nd\Theta}$$

$$R_{CH_4} = \frac{\text{total mols CH}_4 \text{ formed/min x } 10^4}{\text{atom of carbon in bed}} = \frac{N_{CH_4} \text{ x } 10^4}{w_o - \int_o^\Theta Nd\Theta}$$

$$R_C = R_T - 2 R_{CH_4}$$

The carbon oxides rate, R_C, is defined as above because, as will be shown later, the reaction model for methane formation requires that a mol of CO be produced for each mol of methane formed.

N and N_{CH_4} in the above equations are the respective mols of total carbon gases and methane formed per minute from char gasification. They are calculated from the inlet and exit dry gas rates and their compositions at time Θ. W_o is the atoms of carbon in the bed at time $\Theta = 0$, i.e., just after the pretreatment period is completed. The carbon burnoff is calculated from the equation,

$$\% \text{ Burnoff} = \frac{100 \int_o^\Theta Nd\Theta}{W_o}$$

Typical run data and calculations are illustrated in Table II.

Differential rate data are obtained from the two integral rates corresponding to initial char bed weights of 5 and 10 grams by linear extrapolation to zero bed weight.

Integral Rate Data from Continuous Unit

The continuous unit for obtaining integral rate data was described earlier.[4] Two methods of operation were employed. In one, the CO_2 acceptor was circulated through the gasifier. In the other, no acceptor was used. The latter involved operation only of the gasifier, but with continuous feed of hydrodevolatilized char and continuous withdrawal of partially gasified char.

The former operation involved operation of both the regenerator and gasifier vessels. The acceptor was continuously showered through the gasifier bed. The acceptor, segregated in the bottom of the gasifier as a separate phase, was withdrawn continuously and recirculated through the regenerator.

The gasifier was a 4" I.D. vessel and the char bed height was controlled by means of an overflow weir. The bed height in most kinetic runs was 40 inches.

The feedstocks were crushed to -35 mesh and dried with inert gas in a fluid bed at 500°F. The drying was conducted in such a way that almost all the -150 mesh particles were removed by elutriation.

The dried and elutriated feed was then hydrodevolatilized at 1500°F and about one hour residence time in a separate run in the continuous unit. The inlet gas composition was adjusted to simulate that in the corresponding step in the commercial version of the CO_2 acceptor process[3] wherein the partial pressure of hydrogen is about 6 atm. This was done by adding steam and hydrogen and recycling the make gas in the proper proportions.

Analyses of the hydrodevolatilized feedstocks are given in Table Ib.

The composition of the inlet gas during the kinetic runs was controlled by recycle of the product gas. The inlet dry gas was passed through a steam generator in which the water temperature was controlled to give the desired inlet steam partial pressure.

The inventory of carbon in the bed was determined from the bed weight and analysis of the product char. The composition of the product gas was semi-continuously monitored by sampling the dry product gas. Analyses were made with the same gas chromatograph equipment used for the batch kinetics program. The product char was sampled for analysis only when the unit had reached steady state, as evidenced by constant exit gas composition.

The bed weight was determined by ΔP measurement across the fluid bed. The gasification rate was determined from dry exit gas analysis and the metered exit gas rate. The integral gasification rates are then determined as follows when no acceptor is present:

$$R_T = \frac{\text{mols exit gas/min x mol fraction of total carbon x } 10^4}{\text{atom carbon in bed}}$$

$$R_{CH_4} = \frac{\text{mols exit gas/min x mol fraction of } CH_4 \text{ x } 10^4}{\text{atom carbon in bed}}$$

When acceptor was used, correction had to be made in R_T for CO_2 picked up by acceptor. Also, in these instances, CO_2 usually was added to the inlet gas and thus had to be deducted from the total carbon in the outlet gas in calculating R_T.

Results and Discussion

Batch Integral Data

Preliminary experiments showed that the subsequent gasification rates were relatively insensitive to the gas atmosphere or time of pretreatment. The particular procedure used was accepted as a standard because of its simulation of the hydrodevolatilization step in the projected commercial version of the process.

Integral rate data for R_C and R_{CH_4} are shown for several lignite chars in Figures 2 and 3, respectively. All data were obtained at 1500°F and 16 atmospheres total pressure using two different hydrogen steam mixtures in the feed, i.e., 62% H_2-38% H_2O and 32% H_2-68% H_2O. These two values correspond roughly to the H_2/H_2O ratios existing at the top and bottom, respectively, of the projected commercial version of the process. No CO was added and, as we will show later, this strongly inhibits the gasification rates. The rates shown therefore are higher than would be anticipated in practice.

The Renner Cove char is unusual for its high reactivity relative to the other lignite chars. Analyses in Table I show that this lignite is particularly high in sodium. After extraction of 90% of the sodium from this char with hot water, the reaction rates were reduced to a level comparable with those of the other lignite chars. The high reactivity of the Renner Cove char thus may be attributed to a high level of catalysis by sodium.

The high inhibiting effect of H_2 for the carbon oxides rates, R_C, is also noted and is in accord with prior observations on bituminous coal chars.[5] The total gasification rate actually is higher at 1500°F than the rates of gasification of bituminous coal chars previously observed under comparable conditions at 1700°F. Thus, it is clear that lignites are eminently suitable for use in the CO_2 acceptor process from the point of view of reactivity.

.The methane rate, R_{CH_4}, in all cases decreases monotonically with increasing carbon burnoff. The behavior of the carbon oxides rate, R_C, is more complex. It increases with burnoff in most cases at low levels of H_2 inhibition. It tends to show the reverse behavior at high levels of hydrogen inhibition. Although in some cases, a maximum rate is observed at low burnoffs, i.e., up to 35% burnoff.

Differential Rate Data

All the differential rates were obtained with Renner Cove char at 1500°F. The tabulated data for both R_C and R_{CH_4} are given in Table III. These data span the gas compositions to be expected at the top and bottom of the gasifier in the commercial process and for total pressures of 11 and 20 atm. There is one exception, however, in that no CH_4 was added to the inlet gas. Separate runs were, therefore, made to determine the effect of CH_4 inhibition on the rates. These data are given in Table IV.

Correlation of Data

Inspection of the data in Table III clearly shows the strong inhibition by CO on both R_C and R_{CH_4}. To account for the inhibition of the methane formation rate by both CO and CH_4, the following reaction was used as a model to arrive at a suitable correlation.

$$2\ C + H_2 + H_2O\ =\ CH_4 + CO \tag{2}$$
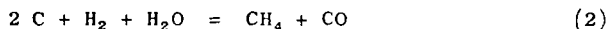
The rate controlling step in the above overall reaction was assumed to be the reaction of absorbed H_2 and H_2O on adjacent carbon sites to produce absorbed oxygen and CH_4.

For the carbon oxides rate, the model reaction was,

$$C + H_2O\ =\ CO + H_2, \tag{3}$$

with the rate controlling step assumed to be the reaction of absorbed H_2O with an adjacent empty carbon site to produce absorbed oxygen and H_2.

Rate equations are readily developed for each case using the standard Langmuir isotherms to represent the fraction of the surface covered with each absorbed gas. The corresponding rate equations are given below:

$$R_C\ =\ \frac{k\left[P_{H_2O} - \dfrac{P_{CO}\,P_{H_2}}{K}\right]}{\left[1 + K_1 P_{H_2O} + K_2 P_{H_2} + K_3 P_{CO}\right]^2} \tag{4}$$

$$R_{CH_4}\ =\ \frac{k'\left[P_{H_2O}P_{H_2} - \dfrac{P_{CH_4}\,P_{CO}}{K}\right]}{\left[1 + K'_1 P_{H_2O} + K'_2 P_{H_2} + K'_3 P_{CO} + K'_4 P_{CH_4}\right]^2} \tag{5}$$

The negative terms in the numerators correspond to the retardation by the reverse reactions.

It is clear from Reaction (2) why R_C is defined as equal to $R_T - 2\ R_{CH_4}$. This is because, by the proposed mechanism, one mol of CO accompanies the formation of every mol of methane.

The constants in the above rate equations were determined from the experimental data using a non-linear least squares technique. The necessary iterative calculations were made with the aid of a digital computer.

The values of the constants thus determined are listed as a function of carbon burnoff in Table V. The agreement between the calculated and observed rates for both R_C and R_{CH_4} is shown in Tables III and IV.

The effect of the reaction, $C + CO_2 = 2\ CO$, on R_C has been neglected in the runs in which CO_2 was a component of the inlet gas. This reaction is slow relative to the steam-carbon reaction and it is strongly inhibited by CO. The data of Blackwood and Ingeme[7] taken on the reaction of CO_2 with a reactive coconut shell charcoal show that, at the conditions used in the present work, much less than 1% of the observed values of R_C could have been contributed by gasification with CO_2.

The correlating equations must be regarded as semi-empirical. The constant, K, in Equation (4) for R_C has values considerably smaller than the equilibrium value of 9.2 at 1500°F for the reaction,

$$\text{graphite} + H_2O = CO + H_2.$$
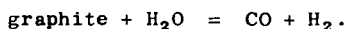
This is unexpected and no explanation is advanced here.

In the methane addition runs, the product, $P_{CO}\ P_{CH_4}$, was too small to allow evaluation of the constant, K', in Equation (5). Therefore, the equilibrium value of 0.388 for the reaction,

$$2\ \text{graphite} + H_2 + H_2O = CH_4 + CO,$$
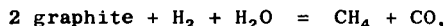
has been assigned tentatively.

If the same active sites are involved in both reactions, then methane should be an inhibitor for the carbon oxides reaction as well as for the methane formation reaction. The data in Table IV show that this is not the case.

Finally, the values of K_1, K_2 and K_3 should be the same as those for K'_1, K'_2 and K'_3. As Table V shows, the values are similar, but not identical.

The effects of the principal variables on the carbon oxides rate, R_C, are illustrated by the curves of Figure 4, derived from Equation (4). The strong inhibiting effects of both H_2 and CO are shown for the 20% burnoff level. Similar effects exist at other burnoff levels. Figure 4 also shows that Equation (4) predicts that the rates go through a maximum with increasing total pressure at constant gas composition. The experimental data of this study do not fall in the region of the maxima. The validity of Equations (4) and (5) has, however, been confirmed by their use to correlate the rate data of the earlier study[5] for bituminous coal char at 1600° and 1700°F with an average deviation of ± 20%. The range of total pressure in the earlier work was 1-30 atm, but the effect of CO on the differential rates was not studied.

The strong inhibition by CO and CH_4 on the rate, R_{CH_4}, is shown in Figure 5 for the 20% burnoff level. As with R_C, similar effects exist at other burnoff levels.

The effects of H_2 and total pressure on R_{CH_4} are illustrated in Figure 6. There is an optimum value of the ratio H_2/H_2+H_2O in the range of 0.4-0.5, depending on the particular values of the other variables. In contrast with R_C, Equation (5) shows that R_{CH_4} continues to increase with increasing total pressure at constant gas composition, but approaches a limiting value beyond the range of the experimental data.

Equation (5) also predicts that R_{CH_4} will decrease to zero with a gas composition of 100% H_2. Actually, considerable gasification does occur at this condition through another reaction, $C + 2\ H_2 = CH_4$. However, a run not otherwise reported here showed that Equation (5) remains valid at values of the ratio H_2/H_2+H_2O up to 0.9.

Integral Rate Data from Continuous Unit

The bulk of the operations in the continuous unit were aimed at a study of operability problems and problems related to handling of the acceptor rather than kinetics. In most cases the feedstocks used were different from the particular lignite (Renner Cove) for which differential rate data were available. Limited operations were, however, carried out with a high sodium lignite (Glenharold) from the same geographical area and from the same Fort Union deposit. Thus, in this case direct comparison with the differential data is possible.

Predictions of integral rate data from differential data is difficult in fluidized systems, since the gas flow pattern is unknown. Complications exist due to gas back mixing and bypassing of the bed by the bubbles which form. It is to be expected, however, that in a smoothly operating fluid bed such as one obtains in pressure operation that the integral rate will lie somewhere between the differential rate predicted for the bottom and top of bed conditions. A summary of the conditions and feedstocks used in the operations and integral rates obtained are given in Table VI.

Unfortunately, a direct comparison between predicted rates from the correlation of differential data is only possible in the case of two of the runs with Glenharold char, i.e., K-1-1 and K-1-2 as shown in Table VII. It is seen that the values of R_C tend to be close to but somewhat higher than the predicted values at the outlet conditions.

A comparison of Run K-1-1 with Run K-1-3 shows the powerful effect of a small increase in temperature of 30°F on rate.

The second group of runs in Table VII shows the effect of using less reactive lignite feedstocks on rate. These runs were made with the acceptor circulating through the bed, which reduces the CO_2 pressure and consequently also the CO pressure by virtue of water-gas-shift reaction. The reduction in inhibiting effect of CO thus compensated for the use of less reactive chars as seen by comparison of Run A-28 (Glenharold char with most of the sodium removed by water washing) with Run K-1-1. The lower reactivity is evidenced, however, by the comparison of the observed rates with those calculated for the more reactive chars. The rates in this case tend to be somewhat lower as expected with one exception (Run A-21) than those calculated even at the outlet conditions.

The results in Tables VI and VII again illustrate the increase in rate effected by reduction in pressure from 20 to 11 atm. They also show the large increase in rate effected by increase in temperature to 1600°F. It should be remarked here, that at 1600°F the operating pressure must be maintained at 20 atm to achieve adequate CO_2 partial pressure for the CO_2 acceptor reaction, even though the rate increases on lowering the pressure.

Data for a few runs with subbituminous chars are given in Table VI. It is seen by a comparison of Runs D-2A and D-2B with Run A24-1 that the reactivity of the subbituminous chars is similar to that of the low-sodium lignite char (Husky II).

A minimum rate for commercial operation is of the order of

$$\frac{50 \times 10^{-4} \text{ lb C gasified/min}}{\text{lb C inventory}}$$

at a steam conversion of about 70%. The results in Table VI indicate, therefore, that for low sodium lignite chars operating temperatures slightly above 1500°F should give adequate rates provided lower pressures of the order of 11 atm are used.

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TABLE Ia

Analyses of Lignite Chars Used in Batch Kinetic Studies

Wt. % Dry Basis	Renner Cove	Dakota Star	South Dakota	Renner Cove Water Extracted	Husky
Hydrogen	1.01	1.10	1.21	--	1.55
Carbon	82.41	83.29	84.00	--	75.18
Nitrogen	.88	.86	.85	--	.82
Oxygen (diff.)	2.03	-.14	.91	--	1.49
Sulfur	.83	1.42	.48	--	2.64
Ash	12.84	13.47	12.52	--	18.96

Ash Composition, Sulfur-Free Basis

Al_2O_3, Wt. %	14.9	10.7	9.3	12.8	10.9
SiO_2	17.6	14.4	33.3	14.1	21.0
Fe_2O_3	8.7	18.1	8.8	10.2	28.1
CaO	26.0	37.5	35.2	35.9	25.7
MgO	9.7	10.6	2.7	14.5	8.9
Na_2O	14.7	3.9	4.3	2.0	.7
K_2O	.5	.2	.5	.04	.2
TiO_2	.5	.3	.7	.7	.5
P_2O_5	.6	.5	.1	.8	.4

TABLE Ib

Analyses of Chars Used in Continuous Gasifier

Wt. % Dry Basis	Glenharold	Glenharold Water Extracted	Husky I	Husky II	Rosebud, Subbituminous
Hydrogen	.73	.75	.94	.86	.87
Carbon	83.16	84.71	82.78	80.68	89.71
Nitrogen	.50	.52	.35	.45	.25
Oxygen (diff.)	1.53	1.49	1.42	1.79	2.04
Sulfur	1.21	.95	1.32	1.47	.18
Ash	12.87	11.58	13.19	14.75	6.95

Ash Composition, Sulfur-Free Basis

Al_2O_3, Wt. %	10.6	11.5	15.6	15.5	26.4
SiO_2	24.4	19.4	24.7	26.0	21.9
Fe_2O_3	8.6	11.8	5.3	5.7	5.8
CaO	33.3	40.1	33.0	35.0	30.8
MgO	7.4	8.7	15.4	11.2	10.2
Na_2O	11.7	5.3	4.3	4.6	2.0
K_2O	.7	.3	.4	.4	.3
TiO_2	.6	.7	1.2	.7	1.0
P_2O_5	.3	.4	.1	.4	.4

TABLE II

Calculations for Typical Run

Run 53:   10 gram Charge, Renner Cove Char, 1500°F, 16.97 atm System Pressure

Inlet Conditions

Dry Gas Rate, SCFH*	7.66	
Steam Rate, SCFH	8.19	

	H_2O	H_2	CO	CH_4	CO_2
Dry Gas Composition, mol %	0	88.93	5.30	0	5.77
Partial Pressures, atm	8.76	7.29	.435	0	.473

Exit Conditions

Elapsed Oxidizing Time, min	0	6	18	30	42	54
Dry Exit Gas Composition						
CO, mol %	–	6.96	6.61	6.20	5.96	5.75
CH_4	–	1.16	.708	.479	.333	.255
CO_2	–	8.20	7.72	7.47	7.15	6.92
H_2 (by diff.)	–	83.69	84.96	85.85	86.56	87.08
Dry Exit Gas Rate, SCFH	–	8.93	8.79	8.38	8.18	8.01
Calculated Quantities						
Rate of Oxygen Appearance in						
Dry Exit Gas, gm O/min	–	.244	.194	.152	.118	.093
Steam Conversion, %	–	9.50	7.55	5.93	4.61	3.62
Wet Exit Gas Composition						
CO, mol %	–	3.80	3.55	3.23	3.05	2.90
CH_4	–	.632	.380	.250	.170	.128
CO_2	–	4.48	4.15	3.89	3.66	3.48
H_2	–	45.73	45.64	44.73	44.28	43.87
H_2O	–	45.35	46.27	47.90	48.84	49.62
Gasification Rate, N,						
gm C gasified/min	.1510	.1384	.1059	.0812	.0624	.0481
Cumulative Carbon Gasified, gm	0	.561	2.019	3.135	3.992	4.652
Instantaneous Wt of C in Bed, W, gm	7.500	6.939	5.481	4.365	3.508	2.848
Integral Total Gasification Rate,						
N/W, gm C gasified/gm C in						
Bed/min x 10^4	201	200	193	186	178	169
Integral Methane Formation Rate,						
gm C gasified/gm C in Bed/						
min x 10^4	38.5	34.9	26.6	21.6	18.2	16.8
Burnoff, % C Gasified	0	7.5	26.9	41.2	53.2	62.0

* Standard conditions are 70°F, 29.92 inches Hg.

TABLE III

Differential Rates for 1500°F Isotherm

Renner Cove Lignite Char

R = lb C Gasif./min/lb C in Bed x 10⁴

$R_T - 2 R_{CH_4} = R_C$

Run No.	Inlet Gas Composition, atm			0% Burnoff			20%			40%			60%		
	H_2O	H_2	CO	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff
42-45	5.58	10.51	1.33	18	16.6	-7.8	34	32.0	-5.9	28	27.2	-2.8	9	8.6	-4.4
46-47	5.42	10.22	1.08	27	29.8	+10.4	41	43.3	+5.6	38	38.2	+0.5	20	20.5	+2.5
50-51	5.47	10.48	.198	95	102	+7.3	106	103	-2.8	94	97.4	+3.6	85	88.4	+4.0
52-53	8.76	7.29	.435	217	222	+2.3	226	231	+2.2	227	225	-0.9	214	209	-2.3
48-49	10.80	5.17	.478	398	388	-0.2	411	410	-0.2	415	412	-0.7	401	402	+0.2
43-44	10.49	5.48	.267	435	425	-0.2	460	446	-3.0	479	451	-5.8	479	446	-6.9
54-57	4.52	6.60	.760	89	83.9	-5.7	93	95.4	+2.6	86	89.0	+3.5	71	71.4	+0.6
55-56	7.36	3.64	0	649.	642	-1.1	667	680	+1.9	691	713	+3.2	709	744	+4.9
				mean		4.4	mean		3.0	mean		2.6	mean		3.2

R_{CH_4}

Run No.	Inlet Gas Composition, atm			0% Burnoff			20%			40%			60%		
	H_2O	H_2	CO	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff
42-45	5.58	10.51	1.33	33	31.4	-4.8	18	19.2	+6.7	11	12.0	+9.1	7	7.8	+11.4
46-47	5.42	10.22	1.08	36	34.4	-4.4	22	21.3	-3.2	13	13.6	+4.6	8	8.9	+11.2
50-51	5.47	10.48	.198	56	57.1	+2.0	38	37.2	-2.1	27	26.1	-3.3	19	18.5	-2.6
52-53	8.76	7.29	.435	50	52.2	+4.4	41	39.3	-4.2	31	29.7	-4.2	24	22.3	-7.1
48-49	10.80	5.17	.478	42	43.6	+3.8	37	36.3	-1.9	31	29.3	-5.5	26	23.5	-9.6
43-44	10.49	5.48	.267	50	50.9	-1.8	40	43.1	+7.8	33	36.1	+9.4	28	29.9	+6.8
54-57	4.52	6.60	.760	29	31.2	-7.6	21	20.3	-3.3	15	13.3	-11.3	11	8.9	-19.1
55-56	7.36	3.64	0	52	47.2	+9.2	44	41.5	-5.7	37	36.6	-1.1	29	32.2	+11.0
				mean		4.8	mean		4.4	mean		6.1	mean		9.8

$$\% \; Diff = 100 \frac{(Calc-obs)}{obs}$$

TABLE IV

CH₄ Addition Runs

					0% Burnoff			20%			40%			60%		
Run Nos.	H_2O	H_2	CO	CH_4	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff	R_{obs}	R_{calc}	% Diff
										$R_T - 2 R_{CH_4} = R_C$						
59-60	5.36	10.55	0	1.32	120	124	+3.2	119	121	+1.6	111	115	+3.4	101	110	+8.2
61-62	5.82	10.13	0.72	1.33	66	62	-6.1	70	71	+1.4	69	65	-5.8	57	50	-12.3
								R_{CH_4}								
59-60	5.36	10.55	0	1.32	32	(1)	-	25.3	(1)	-	18.8	(1)	-	11.6	(1)	-
61-62	5.82	10.13	0.72	1.33	23	23	0	16	17.2	+7.5	11	12	+9.1	8	7.2	-10.0

(1) These data used to calculate K_4 in rate equation.

TABLE V

Tabulated Constants in Rate Equations

R_C

% Burnoff	0	20	40	60
k	576	647	759	934
K	3.26	4.67	4.33	2.92
K_1	.035	.026	.017	.010
K_2	.360	.400	.460	.540
K_3	1.30	1.42	1.63	1.90

R_{CH_4}

	0	20	40	60
k'	15.64	11.51	8.05	5.84
K'	←		.388	→
K_1'	.19	.13	.08	.04
K_2'	.16	.21	.23	.25
K_3'	1.25	1.51	1.80	2.10
K_4	1.18	.88	.81	1.12

TABLE VI

Continuous Unit Gasification Rate Data

Run No.	Temp. °F	Press. atm	Feed-Stock	R_C	R_{CH_4}	% Burn-off	Partial Pressures, atm								lb/hr C Fed	lb C in Bed	Acceptor Present
							Inlet				Outlet						
							H_2O	H_2	CO	CH_4	H_2O	H_2	CO	CH_4			
K1-1	1500	20	(1)	13.2	3.3	17	7.00	5.57	2.22	.83	5.02	6.73	2.69	1.01	4.16	6.03	No
K1-2	1500	20		31.9	5.8	30	8.51	5.62	2.00	.61	5.64	7.28	2.59	.79	4.16	4.78	No
K1-3	1530	20		43.3	7.4	40	8.51	5.60	2.33	.62	4.84	7.65	3.19	.84	4.16	4.70	No
A-28	1500	20	(2)	13.5	6.5	32	5.37	7.43	2.85	.69	4.39	8.71	1.26	.84	1.35	2.74	Yes
A-13	1500	20	(3)	8.2	4.0	39	5.26	7.81	1.36	1.01	3.94	8.48	1.66	1.24	1.31	5.30	Yes
A-21	1500	11	(4)	28.4	4.2	46	4.95	3.34	.88	.20	2.72	4.90	1.48	.33	2.01	4.20	Yes
A-24-1	1600	20		47.9	12.6	42	4.98	6.44	2.37	.83	2.20	7.99	3.32	1.17	4.03	3.83	Yes
A-23-2	1600	11		82.9	7.6	48	5.21	2.53	1.55	.15	1.87	4.25	3.11	.29	4.03	3.28	No
D-2A	1600	20	(5)	29.9	7.4	24	5.43	7.43	2.85	.69	3.08	8.70	3.68	.89	3.40	3.01	No
D-2B	1600	20		47.3	12.1	36	5.35	7.48	2.60	.76	2.82	9.04	3.60	1.05	2.70	2.29	Yes

(1) Glenharold.
(2) Glenharold water extracted.
(3) Husky I.
(4) Husky II.
(5) Rosebud.

TABLE VII

Comparison of Observed and Predicted Rates

Run No.	Temp °F	Press. Atm	Feedstock	Observed Rates		Predicted Rates at 1500°F for Glenharold			
						R_C		R_{CH_4}	
				R_C	R_{CH_4}	Outlet	Inlet	Outlet	Inlet
K1-1	1500	20	Glenharold	13.2	3.3	11	64	5.1	8.1
K1-2	1500	⟶	Glenharold	31.9	5.8	18	96	5.2	9.0
K1-3	1530		Glenharold	43.5	7.4	(1)	74	2.6	6.0
			Water Extracted						
A-28	1500		Glenharold	13.5	6.5	29	66	8.7	12.3
A-13	1500		Husky I	8.2	4.0	9	45	4.3	7.3
A-21	1500	11	Husky II	28.4	4.2	20	192	2.9	7.4

(1) Totally inhibited.

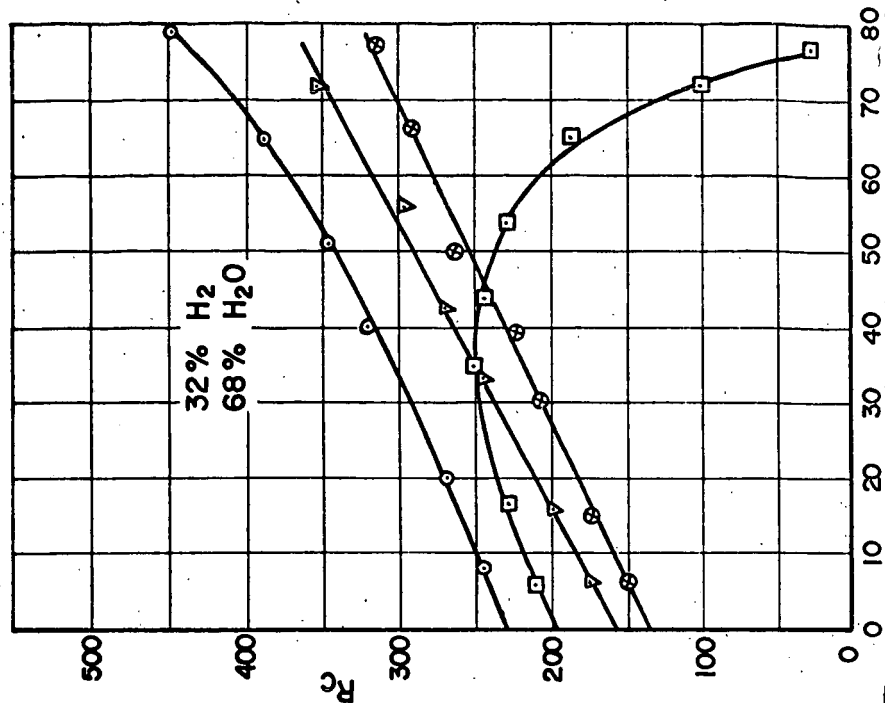SCHEMATIC DIAGRAM

STEAM-CARBON REACTION KINETICS APPARATUS
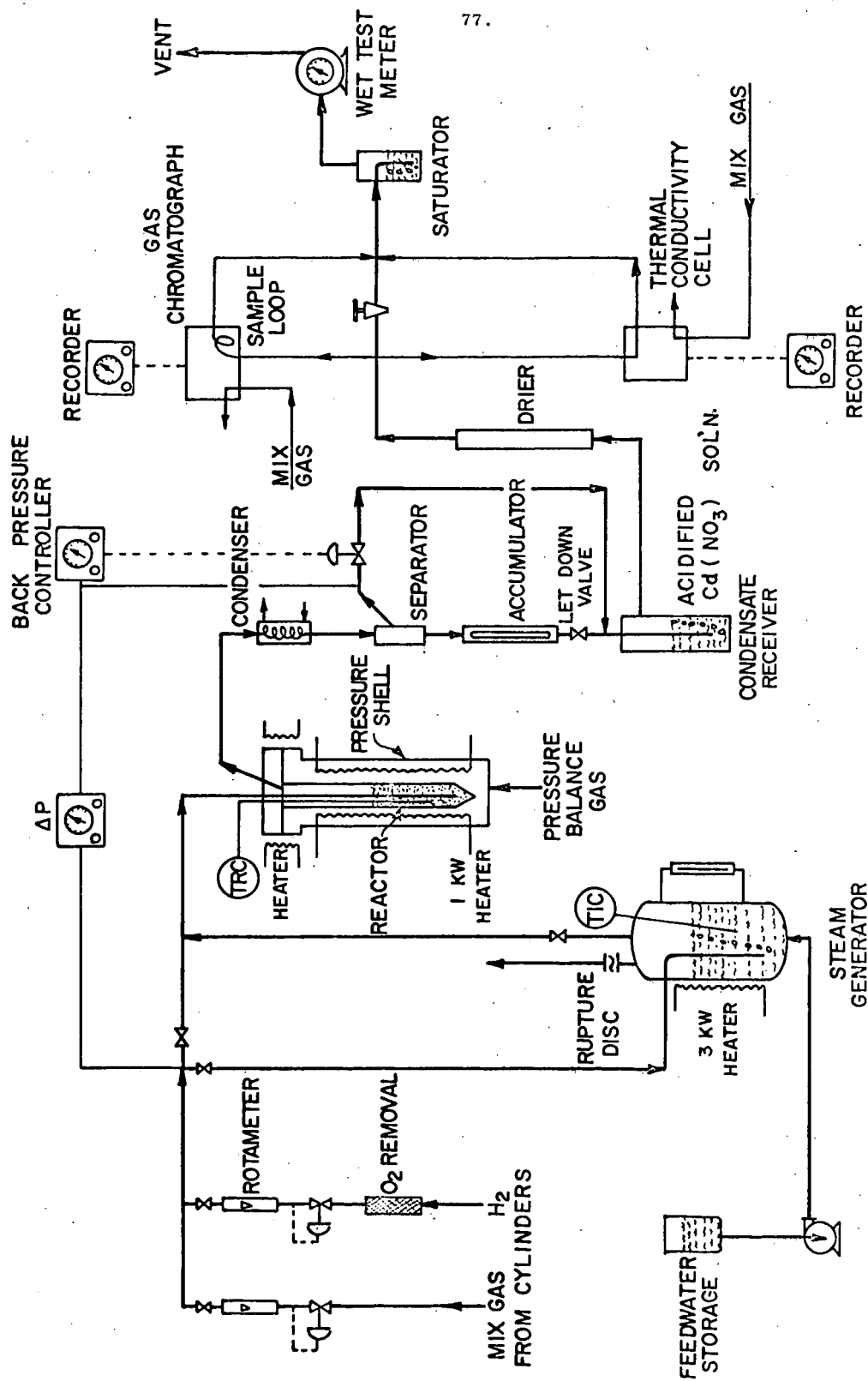
Figure 2

INTEGRAL CARBON OXIDE RATES FOR 10 GRAM CHARGE AT 1500° F

TOTAL PRESSURE, 16 ATM.

⊙ RENNER COVE   ⊗ RENNER COVE, WATER EXTRACTED
▽ DAKOTA STAR   ⊡ SOUTH DAKOTA
✕ HUSKY CHAR

TOTAL PRESSURE, 16 ATM.

⊗ RENNER COVE, WATER EXTRACTED.
□ SOUTH DAKOTA

○ RENNER COVE
▽ DAKOTA STAR
× HUSKY CHAR

32% H₂
68% H₂O

62% H₂
38% H₂O
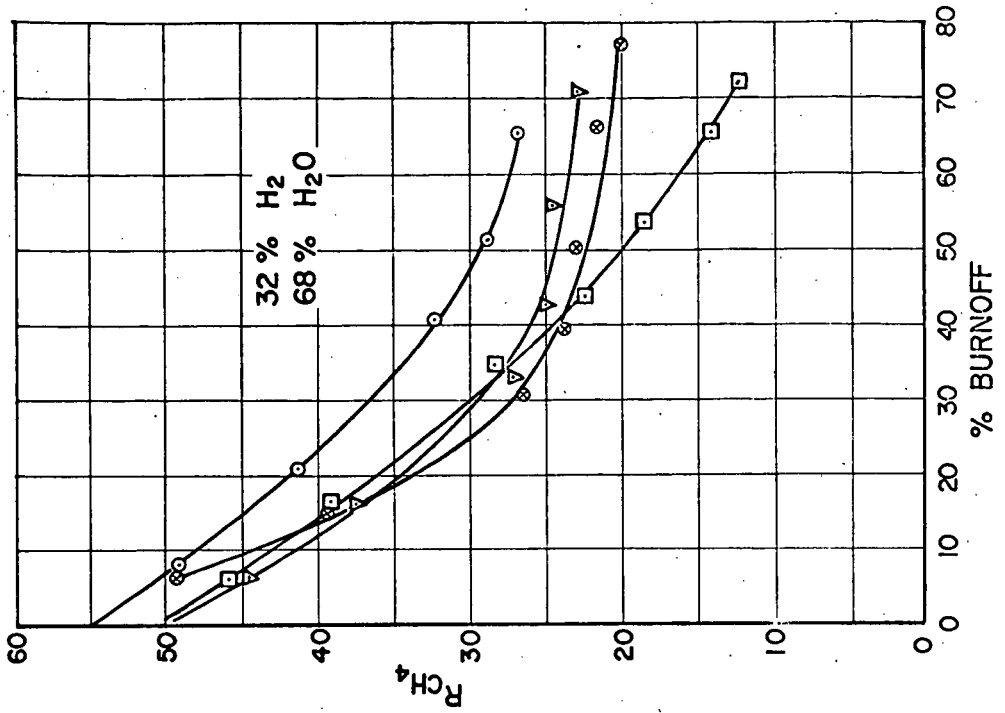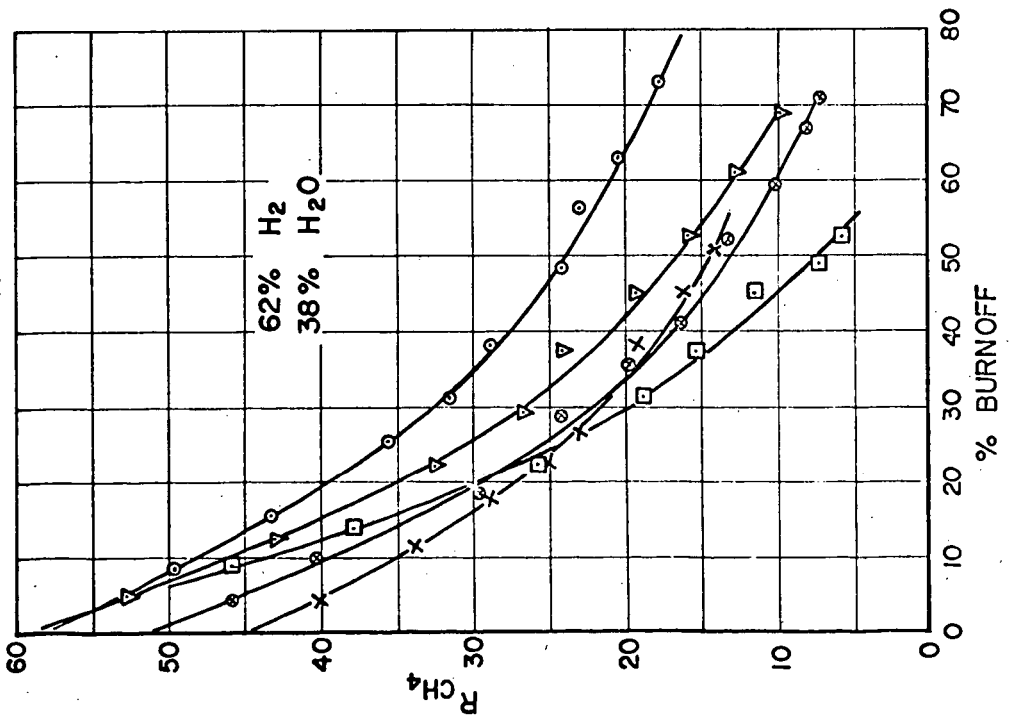
Figure 4

DIFFERENTIAL CARBON·OXIDES GASIFICATION RATES

EFFECTS OF INHIBITION BY H_2 AND CO   AT 20% BURNO

H_2O / H_2

—— 2

---- ½

PARAMETER OF MOL % CO

Rc
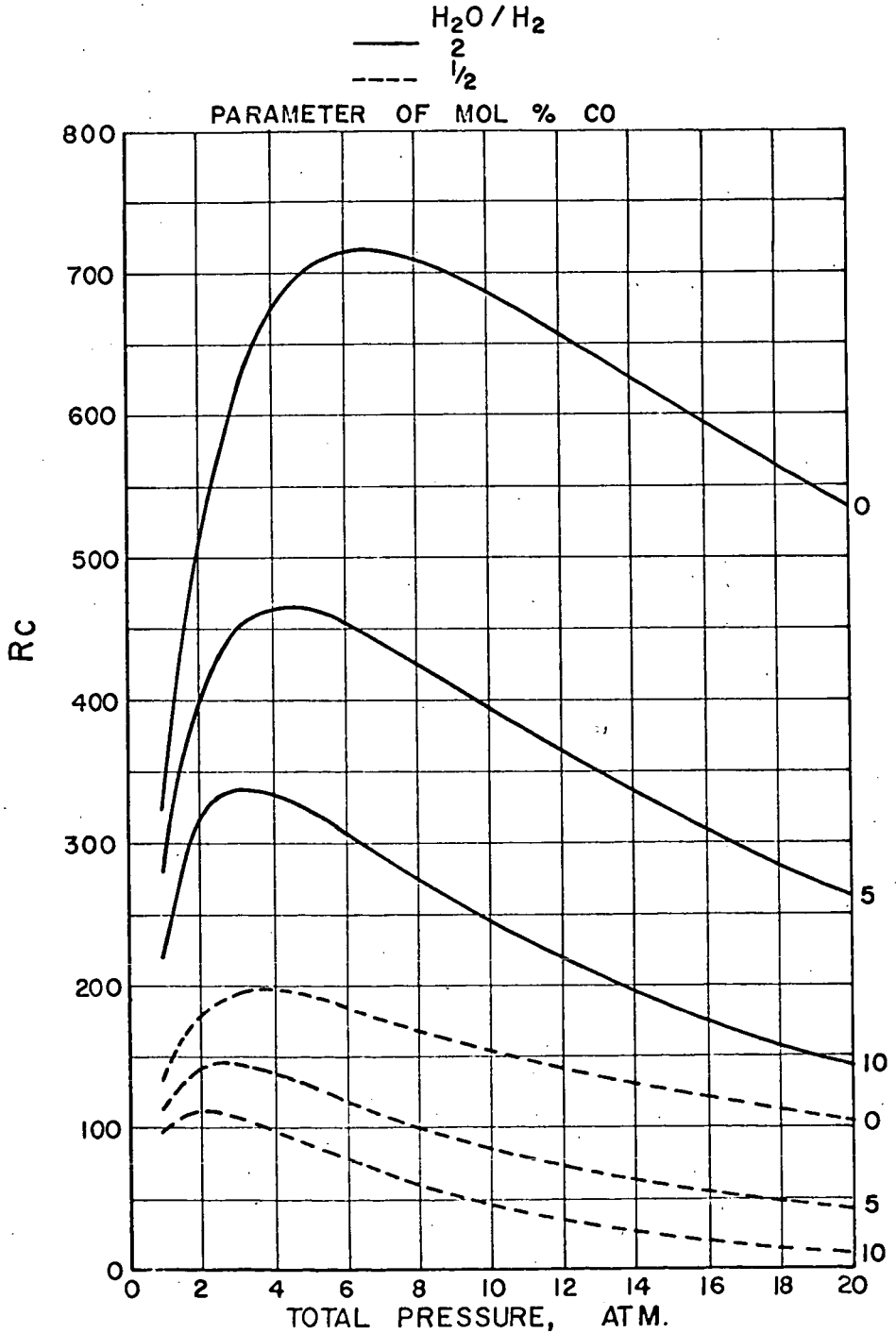
TOTAL PRESSURE,   ATM.

DIFFERENTIAL CH₄ FORMATION RATES

EFFECTS OF INHIBITION BY CO AND CH₄ AT 20% BURNOFF

TOTAL PRESSURE, 20 ATM.
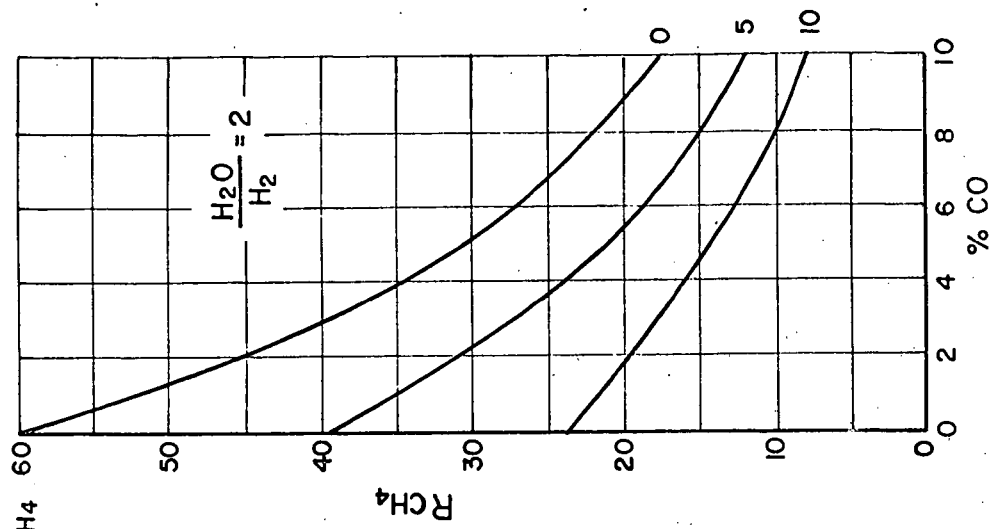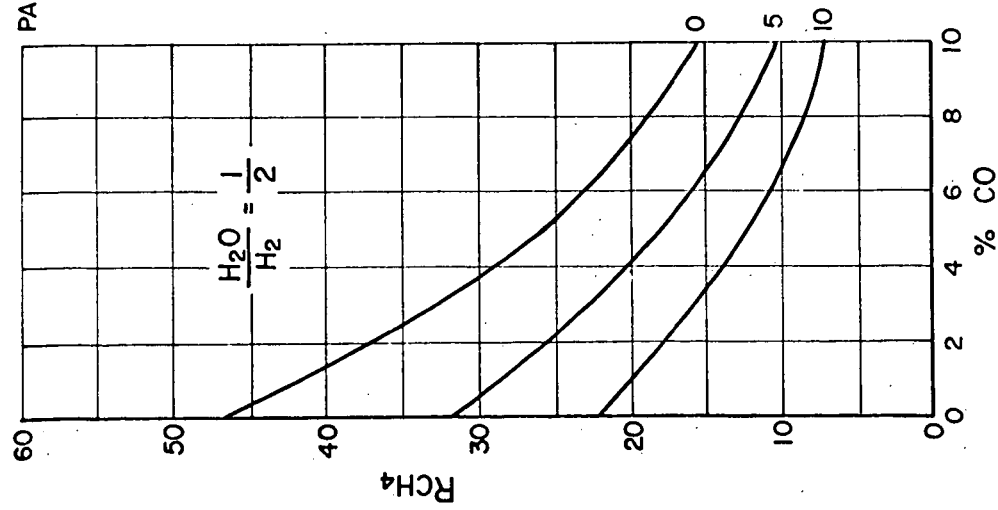

PARAMETER OF MOL % CH₄

82.

Figure 6

DIFFERENTIAL CH₄ FORMATION RATES

EFFECTS OF INHIBITION BY CO AND CH₄ AT 20% BURNOFF